

⑫

**EUROPEAN PATENT APPLICATION**

⑮ Application number: 89810078.9

⑯ Date of filing: 30.01.89

⑰ Int. Cl.<sup>4</sup>: **C 08 L 3/02**  
**C 08 L 101/00**  
**// A61K47/00, A01N25/00**

⑲ Priority: 03.02.88 GB 8802313

⑳ Date of publication of application:  
09.08.89 Bulletin 89/32

㉑ Designated Contracting States:  
AT BE CH DE ES FR GB GR IT LI LU NL SE

㉒ Applicant: **WARNER-LAMBERT COMPANY**  
201 Tabor Road  
Morris Plains New Jersey 07950 (US)

㉓ Inventor: Lay, Gustav  
Schlossstrasse 4  
D-7841 Bad Bellingen (DE)

Rehm, Johannes  
Hofstrasse 7  
D-7812 Bad Krozingen (DE)

Stepro, Robert Frederick Thomas  
20 Gloucester Road  
Poynton Cheshire SK12 1JJ (GB)

Thoma, Markus  
Wendelinsgasse 20  
CH-4125 Riehen (CH)

㉔ Representative: Silbiger, Jakob, Dr.  
c/o CAPSUGEL AG Münchensteinerstrasse 41  
CH-4002 Basel (CH)

㉕ Polymeric materials made from destructurized starch and at least one synthetic thermoplastic polymeric material.

㉖ A blended polymeric material as obtained from a melt comprising a water-containing destructurized starch and at least one essentially water-insoluble synthetic thermoplastic polymer.

**EP 0 327 505 A2**

## Description

**Polymeric materials made from destructurized starch and at least one synthetic thermoplastic polymeric material**

5 The present invention refers to polymeric materials made from destructurized starch and one or more synthetic thermoplastic polymeric materials.

10 It is known that natural starch which is found in vegetable products and which contains a defined amount of water, can be treated at an elevated temperature and in a closed vessel, thereby at elevated pressure, to form a melt. The process is conveniently carried out in an injection molding machine or extruder. The starch is fed through the hopper onto a rotating, reciprocating screw. The feed material moves along the screw towards the tip. During this process, its temperature is increased by means of external heaters around the outside of the barrel and by the shearing action of the screw. Starting in the feed zone and continuing in the compression zone, the particulate feed becomes gradually molten. It is then conveyed through the metering zone, where homogenization of the melt occurs, to the end of the screw. The molten material at the tip can then be treated further by injection molding or extrusion or any other known technique to treat thermoplastic melts, to obtain shaped articles.

15 This treatment, which is described in the European Patent Application No. 84 300 940.8 (Publication No. 118 240) yields an essentially destructurized starch. The reason for this being that the starch is heated above the glass transition and the melting temperatures of its components so that they undergo endothermic transitions. As a consequence a melting and disordering of the molecular structure of the starch granules takes place, so that an essentially destructurized starch is obtained. The expression "destructurized starch" defines starch obtained by such thermoplastic melt formation.

20 The obtained destructurized starch is a new and useful material for many applications. An important property is its biodegradability. In humid air, however, destructurized starch takes up water from the air thereby increasing its own moisture content. In consequence a shaped article made from such destructurized starch loses its form stability very quickly, which is an important disadvantage for many applications. It was found that a shaped article, such as a narrow long rod, under the influence of humid air may shrink within a few hours and lose up to 40 % in its length.

25 Thermoplastic materials must normally be processed in the absence of water or volatile materials. Starch does not melt in the absence of water but decomposes at elevated temperature, i.e. around 240°C. It was therefore assumed that starch could not be used as a thermoplastic component together with hydrophobic water-insoluble polymeric materials such as water insoluble polymeric aminoacids, not only due to the mentioned factors and because starch forms a melt only in the presence of water as described above, but generally due to its chemical structure and its hydrophilic nature.

30 It has now been found that starch, containing a defined amount of water, when heated in a closed vessel as described above to form a melt of destructurized starch, exhibits the same flow characteristics as melts made from thermoplastic synthetic materials with comparable viscosity values and that melts made from water-containing destructurized starches are compatible in their processing with melts formed by essentially water insoluble anhydrous thermoplastic synthetic polymers. In this sense the two types of molten materials show an interesting combination of their properties, especially after the melt has solidified.

35 One very important aspect is the surprisingly improved dimensional stability of such destructurized starch blended with such a thermoplastic synthetic material. For example, by blending destructurized starch with only 1 % by weight of a thermoplastic synthetic polymer as described later on, a shrinkage of less than 4 % is observed after two days, for the narrow long rod just mentioned above.

40 The present invention refers to blended polymeric materials as obtained from a melt comprising a water-containing destructurized starch and at least one essentially water insoluble synthetic thermoplastic polymer.

45 The present invention refers to said blended polymeric materials in the molten or in the solid form.

The present invention further refers to shaped articles made from said blended polymeric material.

50 The present invention further refers to a method of producing said blended polymeric materials in the molten or solid form as well as a method of producing shaped articles from said polymeric materials.

55 Specifically the present invention also refers to a method of producing polymeric materials comprising a modified destructurized starch and an essentially water insoluble synthetic thermoplastic polymer by heating starches having a water content of 5 to 30 % by weight based on the starch/water component in a closed volume to elevated temperatures thereby at elevated pressures for a time long enough to form a melt, characterized in that said starch/water material is mixed with at least one essentially water-insoluble synthetic thermoplastic polymer before or during melting formation. Preferably the synthetic thermoplastic polymer is added before melting is initiated.

60 The term "starch" as used herein includes chemically essentially non-modified starches as for example generally carbohydrates of natural, vegetable origin, composed mainly of amylose and/or amylopectin. They may be extracted from various plants, examples being potatoes, rice, tapioca, corn (maize) and cereals such as rye, oats, wheat. Preferred is starch made from potatoes, corn or rice. It further includes physically modified starches such as gelatinized or cooked starches, starches with a modified acid value (pH), e.g. where acid has been added to lower their acid value to a range of about 3 to 6. Further included are starches, e.g. potato

starch, in which the divalent ions like  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$ -ions bridging the phosphate groups have been partially or completely eliminated from this bridging function, i.e. the phosphate bridges have partially or completely been broken down and optionally wherein the eliminated ions have been replaced again partially or wholly by the same or different mono- or polyvalent ions. It further includes pre-extruded starches.

It has recently been found, that starches with a water content within the range of about 5 to about 40% by weight based on the weight of the composition undergo a "specific narrow endothermic transition" on heating to elevated temperatures and in a closed volume just prior to its endotherm change characteristic of oxidative and thermal degradation. The specific endothermic transition can be determined by differential scanning calorimetric analysis (DSC) and is indicated on the DSC-diagram by a specific relatively narrow peak just prior to the endotherm characteristic of oxidative and thermal degradation. The peak disappears as soon as the mentioned specific endothermic transition has been undergone. The term "starch" includes also treated starches wherein said specific endothermic transition has been undergone.

Examples of water-insoluble thermoplastic materials are polyolefines, such as polyethylene (PE), polyisobutylenes, polypropylenes, vinylpolymers such as poly(vinyl chloride) (PVC), poly(vinyl acetates), polystyrenes; polyacrylonitriles (PAN); polyvinylcarbazols (PVK); essentially water-insoluble poly(acrylic acid) esters or poly(methacrylic acid) esters; polyacetals (POM); polycondensates such as polyamides (PA), thermoplastic polyesters, polycarbonates, poly(alkylene terephthalates); polyarylethers; thermoplastic polyimides; but also poly(hydroxy butyrate) (PHB) and high molar-mass, essentially water-insoluble poly(alkylene oxides) such as polymers of ethylene oxide and propylene oxide as well as their copolymers are included.

Further included are essentially water-insoluble thermoplastic copolymers of the different kinds known such as ethylene/vinyl acetate-copolymers (EVA); ethylene/vinyl alcohol-copolymers (EVAL); ethylene/acrylic acid-copolymers (EAA); ethylene/ethyl acrylate-copolymers (EEA); ethylene/methyl acrylate-copolymers (EMA); ABS -copolymers; styrene/acrylonitrile-copolymers (SAN); as well as their mixtures.

Preferred from these are those with a set processing temperature preferably within the range of 95°C to 210°C, preferably within the range of 95°C to 190°C.

Preferred from these are further those polymers containing polar groups such as ether-, acid or ester groups. Such polymers include e.g. copolymers of ethylene, propylene or isobutylene such as ethylene/vinyl acetate-copolymers (EVA), ethylene/vinyl alcohol-copolymers, ethylene/acrylic acid-copolymers (EAA), ethylene/ethyl acrylate-copolymers (EEA), ethylene/methacrylate-copolymers (EMA), styrene/acrylonitrile-copolymers (SAN); polyacetals (POM) and their mixtures as mentioned above.

The ratio of the water containing destructurized starch to synthetic polymer can be 0.1:99.9 to 99.9:0.1. It is however preferred that the destructurized starch contributes noticeably to the properties of the final material. Therefore, it is preferred that the destructurized starch is present in an amount of at least 50% and more preferably in the range of 70% to 99.5% by weight of the entire composition, i.e. the synthetic polymer is present in a concentration of less than 50 % and more preferably in a concentration in the range of 30 % to 0.5 % by weight of the entire composition.

A mixture of 0.5 to 15% by weight of the synthetic polymer and 99.5 to 85% of the water containing destructurized starch shows already a significant improvement in the properties of the obtained materials. For certain applications a ratio of the synthetic polymer to the starch/water component of 0.5 - 5% to 99.5 - 95% is preferred and especially a ratio of 0.5 - 2% to 99.5 - 98% by weight.

The synthetic polymer may contain the usual known additives for processing.

The starch is preferably destructurized and granulated before it is mixed with the synthetic polymer which is preferably granulated to an equal granular size as the destructurized starch. However, it is possible to process native starch or pre-extruded granulated or powdered starch together with powdered or granulated plastic material in any desired mixture or sequence.

The essentially destructurized starch/water composition or granules have a preferred water content in the range of about 10 to 20% by weight of the starch/water component, preferably 12 to 19% and especially 14 to 18% by weight of the starch/water component.

The water content herein refers to the weight of starch/water component within the total composition and not to the weight of the total composition which would include also the weight of the essentially water-insoluble synthetic thermoplastic polymer. It is essential that the starch/water component has the indicated water content during melt formation.

As an "essentially water-insoluble synthetic thermoplastic polymer" a polymer is understood which preferably dissolves water at a rate of maximum 5% per 100 grams of the polymer at room temperature and preferably at a rate of maximum about 2% per 100 grams of the polymer at room temperature.

In order to destructurize the starch, it is suitably heated in a screw barrel of an extruder for a time long enough to effect destructurization. The temperature is preferably within the range of 105°C to 190°C, preferably within the range of 130°C to 190°C depending on the type of starch used. For this destructurizing, the starch material is heated preferably in a closed volume. A closed volume can be a closed vessel or the volume created by the sealing action of the unmolten feed material as happens in the screw of injection molding or extrusion equipment. In this sense the screw and barrel of an injection molding machine or an extruder is to be understood as being a closed vessel. Pressures created in a closed vessel correspond to the vapour pressure of water at the used temperature but of course pressure may be applied and/or generated as normally occurs in a screw and barrel. The preferred applied and/or generated pressures are in the range of

pressures which occur in extrusion and are known per se, i.e. from zero to  $150 \times 10^5$  N/m<sup>2</sup> preferably from zero to  $75 \times 10^5$  N/m<sup>2</sup> and most particularly from zero to  $50 \times 10^5$  N/m<sup>2</sup>. The obtained destructurelized starch is granulated and ready to be mixed with the synthetic polymer to obtain the granular mixture of the destructurelized starch/synthetic polymer starting material to be fed to the screw barrel.

5 Within the screw, the granular mixture is heated to a temperature which is generally within the range of about 80°C to 200°C, preferably within the range of about 120°C to 190°C and especially within the range of about 130°C to 190°C.

The minimum pressures under which the melts are formed correspond to the water vapour pressures produced at said temperatures. The process is carried out in a closed volume as explained above, i.e. in the range of the pressures which occur in extrusion or injection molding processes and known per se, e.g. from zero to  $150 \times 10^5$  N/m<sup>2</sup> preferably from zero to  $75 \times 10^5$  N/m<sup>2</sup> and most particularly from zero to  $50 \times 10^5$  N/m<sup>2</sup>.

When forming a shaped article by extrusion the pressures are preferably as mentioned above. If the melt according to this invention is, e.g., injection molded, the normal range of injection pressures used in injection molding is applied, namely from  $300 \times 10^5$  N/m<sup>2</sup> to  $3.000 \times 10^5$  N/m<sup>2</sup> and preferably from  $700 \times 10^5$  to  $2200 \times 10^5$  N/m<sup>2</sup>.

The starch material of the present invention may contain or may be mixed with additives such as extenders, fillers, lubricants, plasticizers and/or colouring agents.

The additives may be added before the destructurelizing step or after this step, i.e. mixed with the solid granules of the destructurelized starch. It mainly depends on the intended use of the destructurelized starch.

20 Such additives are extenders of different kinds, e.g. gelatin, vegetable proteins such as sunflower protein, soybean proteins, cotton seed proteins, peanut proteins, rape seed proteins, blood proteins, egg proteins, acrylated proteins; water-soluble polysaccharides such as: alkylcelluloses hydroxyalkylcelluloses and hydroxyalkylalkylcelluloses, such as: methylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxyethylmethylcellulose, hydroxypropylmethylcellulose, hydroxybutylmethylcellulose, cellulose esters and hydroxyalkylcellulose esters such as: cellulose acetylphthalate (CAP), Hydroxypropylmethylcellulose (HPMCP); carboxyalkylcelluloses, carboxyalkyl-alkylcelluloses, carboxyalkylcellulose esters such as: carboxymethylcellulose and their alkali-metal salts; water-soluble synthetic polymers such as: poly(acrylic acids) and their salts and essentially water soluble poly(acrylic acid) esters, poly(methacrylic acids) and their salts and essentially water-soluble poly(methacrylic acid) esters, essentially water soluble poly(vinyl acetates), poly(vinyl alcohols), poly(vinyl acetate phthalates) (PVAP), poly(vinyl pyrrolidone), poly(crotonic acids); suitable are also phthalated gelatin, gelatin succinate, crosslinked gelatin, shellac, water soluble chemical derivatives of starch, cationically modified acrylates and methacrylates possessing, for example, a tertiary or quaternary amino group, such as the diethylaminoethyl group, which may be quaternized if desired; and other similar polymers.

35 Such extenders may optionally be added in any desired amount preferably up to and including 50 %, preferably within the range of 3 % to 10 % based on the total weight of all the components.

Further additives are inorganic fillers, such as the oxides of magnesium, aluminum, silicon, titanium, etc. preferably in a concentration in the range of about 0.02 to 3 % by weight preferably 0.02 to 1 % based on the total weight of all the components.

40 Further examples of additives are plasticizers which include low molecular poly(alkylene oxides), such as poly(ethylene glycols), poly(propylene glycols), poly ethylene-propylene glycols; organic plasticizers of low molar masses, such as glycerol, glycerol monoacetate, diacetate or triacetate; propylene glycol, sorbitol, sodium diethylsulfosuccinate, triethyl citrate, tributyl citrate, etc., added in concentrations ranging from 0.5 to 15 %, preferably ranging from 0.5 to 5 % based on the total weight of all the components.

45 Examples of colouring agents include known azo dyes, organic or inorganic pigments, or colouring agents of natural origin. Inorganic pigments are preferred, such as the oxides of iron or titanium; these oxides, known per se, being added in concentrations ranging from 0.001 to 10 %, preferably 0.5 to 3 %, based on the total weight of all the components.

50 The sum of the plasticizer and water contents should preferably not exceed 25 %, and should most preferably not exceed 20 %, based on the total weight of all the components.

There may further be added compounds to improve the flow properties of the starch material such as animal or vegetable fats, preferably in their hydrogenated form, especially those which are solid at room temperature. These fats have preferably a melting point of 50°C or higher. Preferred are triglycerides of C<sub>12</sub> -, C<sub>14</sub> -, C<sub>16</sub> -, and C<sub>18</sub> - fatty acids.

55 These fats can be added alone without adding extenders or plasticizers.

These fats can advantageously be added alone or together with mono- and/or diglycerides or phosphatides, especially lecithin. The mono- and diglycerides are preferably derived from the types of fats described above, i.e. from C<sub>12</sub> -, C<sub>14</sub> -, C<sub>16</sub> -, and C<sub>18</sub> - fatty acids.

60 The total amounts used of the fats, mono-, diglycerides and/or lecithins are up to 5 % and preferably within the range of about 0.5 to 2 % by weight of the destructurelized starch components.

The materials described herein above form thermoplastic melts on heating and in a closed vessel, i.e. under conditions of controlled water-content and pressure. Such melts can be processed just like conventional thermoplastic materials, using, for example, injection molding, blow molding, extrusion and coextrusion (rod, pipe and film extrusion), compression molding, to produce known articles. The articles include bottles, sheets, 65 films, packaging materials, pipes, rods, laminated films, sacks, bags, pharmaceutical capsules, granules or

powders.

Such modified starches may be used as carrier materials for active substances, and may be mixed with active ingredients such as pharmaceuticals and/or agriculturally active compounds such as insecticides or pesticides for subsequent release applications of these ingredients. The resulting extruded materials can be granulated or worked to fine powders.

The following examples further explain the invention.

#### Example 1

##### (a) Preparation of destructurelized starch granulates.

Natural potato starch, a lubricant/release agent (hydrogenated fat) and a melt flow accelerator (lecithin) and titanium dioxide were mixed together in the relative proportions in a powder mixer for 10 minutes so that a composition consisting of 80.6 parts of natural potato starch, one part of the hydrogenated triglyceride of the fatty acid C<sub>18</sub>:C<sub>16</sub>:C<sub>14</sub> in a ratio of 65:31:4 weight percent, 0.7 parts lecithin, 0.7 parts of titanium dioxide and 17 parts water in the form of a freely flowing powder is obtained. This material was then fed to the hopper of an extruder. In the screw barrel the powder was melted. The temperature within the barrel was measured to be 175°C, the average total residence time was 12 minutes approx. 10 minutes heating time, approx. 2 minutes in molten state) and the pressure generated was equal to the vapour pressure of the moisture present in the volume of the extruder barrel. The melt was then extruded, and cut into granulates of an average diameter of 2 to 3 mm. The material was hard, white with a fine foamed structure. The water content was 120%, as water was allowed to escape when the melt left the extruder nozzle.

The obtained granulated material was then conditioned to a water content of 170%.

##### (b) Preparation of destructurelized starch granules of acid-washed potato starch.

600 g of native potato starch were suspended in 700 cm<sup>3</sup> of 0.2M HCl and stirred for 10 minutes. The suspension was filtered and the starch washed on the filter three times with 200 cm<sup>3</sup> portions of 0.2M HCl. The starch was again suspended in 500 cm<sup>3</sup> 0.2M HCl, stirred again for 10 minutes, filtered, washed three times with 200 cm<sup>3</sup> portions of 0.2M HCl.

After the treatment with HCl, the excess of acid was removed by washing on a filter with demineralized (deionized) water in the following way: the starch was washed twice with 200 cm<sup>3</sup> portions of deionized water and then suspended in 500 cm<sup>3</sup> of deionized water. This washing procedure with deionized water (to remove excess acid) was repeated twice to get the starch free of HCl. This was controlled by adding silver nitrate to the washing water. When there was no more silver chloride precipitating in the washing water, the washing was completed. The washed starch was pressed on the filter and dried in a conditioning room (25°C, 40% RH) until it equilibrated at about 17.0% H<sub>2</sub>O.

Analyses have been carried out before and after the acid washing of starch for mono- and divalent ions and results obtained showed that the Ca<sup>2+</sup>-ions bridging the phosphate groups were essentially removed.

##### (c) Injection molding of a mixture of destructurelized starch and synthetic polymer.

The granulates as obtained under (a) and the granules as obtained under (b) above were mixed with a synthetic polymer in the weight ratios as specified in table 1 below and injection molded to produce test pieces suitable for measuring their dimensional stability. The test pieces were injection molded using a Kloeckner FM60 injection molding machine at an injection molding temperature at the end of the barrel of 165°C at a cycle time of about 15 seconds. The injection molding pressure was about 1600 bars and the back pressure about 75 bars.

##### d) Testing and testing conditions

The test pieces were placed (laid on a screen) in a climatic cabinet in which a high relative humidity (near 100% R.H.) was maintained using a 1% aqueous sulfuric acid solution at room temperature. For each blends material 3 test pieces were used to obtain average figures relating to dimensional stability.

The test pieces obtained from the mold, were cut to a length of about 87-90 mm, which is close to the optimal length which can be measured on a NIKON profile projector V12.

After cutting the length, the samples were initially equilibrated to 14% H<sub>2</sub>O content, placed on the NIKON V12 and their widths and lengths were measured.

The samples were then placed in the climatic cabinet and exposed to a high relative humidity at room temperature. Reference samples of unblended starch were placed under same conditions. The dimensions were measured on each of the 3 pieces and recorded after 1, 2 and 3 days.

The lengths measured are given in Table 1.

In width, slight expansions of up to 4% with 1% polymer content and less than 4% with 5% polymer, were generally observed.

The Figures 1, 2, 3 and 4 illustrate the results obtained according to this Example for storing three days under the indicated conditions.

Figure 1 shows comparative test results for untreated starch, blended starch containing 1% of polyethylene and 5% of polyethylene when stored three days according to Example 1(d).

Figure 2 shows comparative test results for untreated starch, blended starch containing 1% of

polyacetal and 5% of polyacetal when stored three days according to Example 1(d).

Figure 3 shows comparative test results for untreated starch, blended starch containing 1% of EAA (ethylene/acrylic acid-copolymer) and 5% of EAA (ethylene/acrylic acid-copolymer) when stored three days according to Example 1(d).

Figure 4 shows comparative test results for untreated starch, blended starch containing 1% of EVA (ethylene/vinyl acetate-copolymer) and 5% of EVA (ethylene/vinyl acetate-copolymer) when stored three days according to Example 1(d).

TABLE 1

No.	polymer added	% by weight of polymer added	dimensional deformation, change in % after,		
			1 day	2 days	3 days
1.	none, comparative example		- 40	- 50.1	- 54
2.	polyethylene	0.5	- 15	- 20	- 25
3.	"	1.0	- 13	- 14	- 17
4.	"	5.0	+ 1.3	+ 0.2	- 1.8
5.	polystyrene	1.0	+ 1.05	- 0.5	- 6.7
6.	"	5.0	+ 0.45	- 0.3	- 0.8
7.	polyacetal	0.1	± 1	- 4.0	- 10
8.	"	1.0	+ 1.5	+ 0.4	- 6.2
9.	"	5.0	+ 0.7	+ 0.1	- 0.6
10.	"	10.0	± 0.1	± 0.1	± 0.1
11.	"	20.0	± 0.1	± 0.1	± 0.1
12.	EAA*	0.5	- 0.2	- 7.0	- 18.0
13.	"	1.0	+ 0.07	- 4.0	- 11.0
14.	"	5.0	+ 0.6	- 1.4	- 5.0
15.	"	10.0	+ 0.1	- 0.1	- 0.4
16.	EVA**	0.5	- 0.5	- 5.0	- 17.1
17.	"	1.0	+ 0.3	- 0.5	- 7.0
18.	"	5.0	+ 0.2	- 1.2	- 4.8
19.	"	20.0	- 0.1	- 0.1	- 2.0

\* EAA = ethylene/acrylic acid-copolymer (9% acrylic acid comonomer)

\*\* EVA = ethylene/vinyl acetate-copolymer (10% vinyl acetate comonomer)

#### Example 2

The granulates obtained according to Example 1(a) and the granules obtained according to Example 1(b) where each mixed with polyethylene, polystyrene, polyacetal, ethylene/acrylic/acid-copolymers (9% acrylic acid-comonomer) and ethylene/vinyl acetate-copolymer (10% vinyl acetate-comonomer) each time in ratio of 25%, 50%, 75% and 90% by weight of polymer added. Dimensional changes were nominal after exposure to humid air according to Example 1(d).

#### Claims

1. A blended polymeric material as obtained from a melt comprising a water-containing destructurelized starch and at least one essentially water-insoluble synthetic thermoplastic polymer.

2. A polymeric material according to claim 1, wherein the thermoplastic polymer is selected from the group consisting of polyolefines, vinylpolymers, polyacetals (POM); polycondensates, thermoplastic polyesters, polycarbonates, poly(alkylene terephthalates); polyarylethers; thermoplastic polyimides; polyhydroxybutyrate (PHB) and high molecular weight essentially water-insoluble polyalkylene oxides or copolymers thereof.

3. A polymeric material according to claim 2, wherein the thermoplastic polymer is selected from the group consisting of polyethylene (PE), polyisobutylenes, polypropylenes, poly(vinyl chloride) (PVC), poly(vinyl acetates), polystyrenes, polyacrylonitriles (PAN), polyvinylcarbazols (PVK), polyamides (PA), essentially water-insoluble poly(acrylic acid esters) and essentially water-insoluble poly(methacrylic acid esters), as well as their copolymers and their mixtures.

4. A polymeric material according to claim 2, wherein the thermoplastic polymer is selected from the group consisting of ethylene/vinyl acetate-copolymers (EVA), ethylene/vinyl alcohol-copolymers (EVAL), ethylene/acrylic acid-copolymers (EAA), ethylene/ethyl acrylate-copolymers (EEA), ethylene/methyl

acrylate-copolymers (EMA), ABS-copolymers, styrene/acrylonitrile-copolymers (SAN), polyacetals and their mixtures.

5. A polymeric material according to anyone of the claims 1 to 4, wherein the ratio of the water-containing destructurized starch to synthetic polymer is 0.1:99.9 to 99.9:0.1, preferably wherein the water-containing starch is present in an amount of at least 50% and more preferably in the range of 70 to 99% by weight of the entire composition. 5

6. A polymeric material according to anyone of the claims 1 to 4, wherein the ratio of the synthetic polymer to the starch/water component is 0.5 - 5% to 99.5 - 95% by weight and preferably from 0.5% - 2% to 99.5% - 98% by weight.

7. A polymeric material according to anyone of the claims 1 to 6, wherein said starch is selected from chemically essentially non-modified starch being carbohydrates of natural, vegetable origin composed mainly of amylose and/or amylopectin, preferably potatoes, rice, tapioca, corn, rye, oats, wheat; physically modified starch; starch with a modified acid value (pH); starch, in which the divalent ions bridging the phosphate groups have been eliminated from this bridging function and optionally wherein the eliminated ions have been replaced again partially or wholly by the same or different mono- or polyvalent ions, and/or pre-extruded starches. 10 15

8. A polymeric material according to anyone of the claims 1 to 7, wherein said starch mixed with at least one synthetic polymer was heated for destructurization in a closed volume for a time long enough to effect destructurization to a temperature within the range of about 105°C to 190°C, preferably within the range of 130°C to 190°C. 20

9. A polymeric material according to anyone of the claims 1 to 8, wherein for destructurization pressure was applied in the range of from zero to  $150 \times 10^5$  N/m<sup>2</sup>, preferably from zero to  $75 \times 10^5$  N/m<sup>2</sup> and particularly from zero to  $50 \times 10^5$  N/m<sup>2</sup>. 25

10. A polymeric material according to anyone of the claims 1 to 9, wherein the starch has a water content in the range of about 10 to 20% by weight of the starch/water component, preferably 12% to 19% and especially 14% to 18% by weight, calculated to the weight of the starch/water component. 30

11. A polymeric material according to anyone of the claims 1 to 10, wherein the starch/synthetic polymer mixture contains extenders, fillers, lubricants, plasticizers and/or coloring agents.

12. A polymeric material according to claim 11, characterized in that there is added at least one extender or a mixture of extenders within the range of up to 50%, preferably within the range of 3% to 10%, based on the weight of all components. 35

13. A polymeric material according to claims 11 or 12, characterized in that there is added at least one organic filler or a mixture of such fillers in a concentration of about 0.02 to 3%, preferably 0.02 to 1%, by weight of all components.

14. A polymeric material according to anyone of the claims 11 to 13, wherein there is added a plasticizer within the range of about 0.5 to 15%, preferably 0.5 to 5% by weight of all components. 40

15. A polymeric material according to anyone of the claims 11 to 14, wherein a coloring agent is added in a concentration of about 0.001 to 10%, preferably 0.5 to 3% by weight of all components.

16. A polymeric material according to anyone of the claims 11 to 15, wherein a plasticizer is added and the sum of the plasticizer and water contents does not exceed 25%, and preferably does not exceed 20% by weight of all components. 45

17. A polymeric material according to anyone of the claims 1 to 16, wherein the blended starch contains at least one active ingredient selected from pharmaceuticals and/or agriculturally active compounds.

18. The polymeric material in the form of a melt obtained according to anyone of the claims 1 to 17.

19. The solidified destructurized blended starch obtained by cooling the material obtained according to claim 18. 50

20. A method of producing a polymeric material as claimed in anyone of the claims 1 to 18 comprising a modified destructurized starch and an essentially water-insoluble synthetic thermoplastic polymer by heating a starch having a water content of 5 to 30% by weight based on the starch/water component in a closed volume to elevated temperatures thereby at elevated pressures for a time long enough to form a melt, characterized in that said starch/water material is mixed with at least one essentially water-insoluble synthetic thermoplastic polymer before or during melting formation. 55

21. The use of modified starch/synthetic polymer mixture compositions obtained as claimed in anyone of the claims 1 to 19 as carrier material for active ingredients, preferably as carrier materials for pharmaceuticals, and/or agriculturally active substances. 60

22. The process of shaping a destructurized starch/synthetic polymer mixture composition as obtained according to anyone of the claims 1 to 18, under controlled water content and pressure conditions as a thermoplastic melt wherein said shaping process is at least one member selected from the class consisting of injection molding, blow molding, extrusion and coextrusion, compression molding or vacuum forming. 65

23. Shaped articles produced from a composition as claimed in anyone of the claims 1 to 18.

24. The articles of claim 23, wherein said articles have been shaped as bottles, sheets, films, packaging materials, pipes, rods, laminates, sacks, bags or pharmaceutical capsules, granules or powders.

**Fig. 1**

Comparative Testing, unblended starch versus starch blended with:

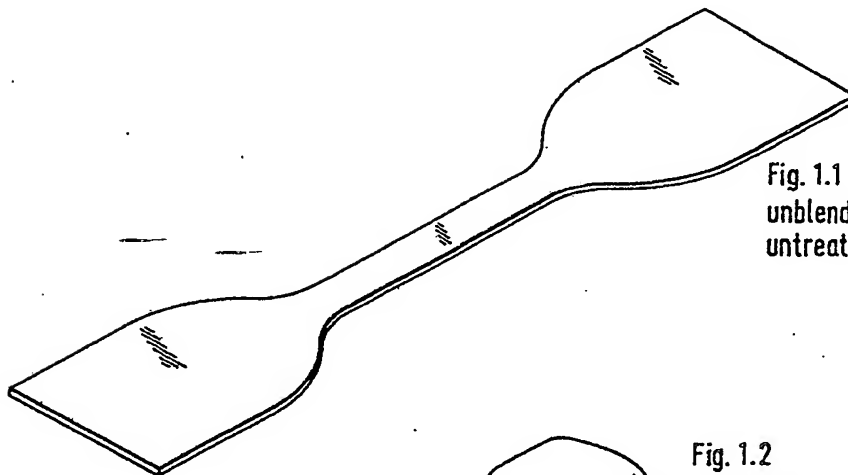


Fig. 1.1  
unblended or blended,  
untreated

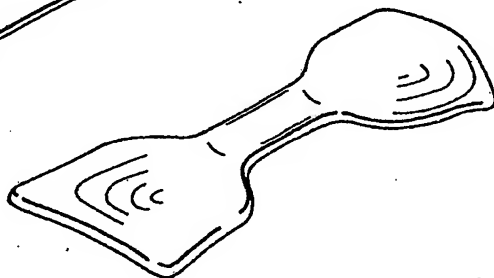


Fig. 1.2  
unblended,  
treated according to  
Table 1, No. 1 after  
3 days

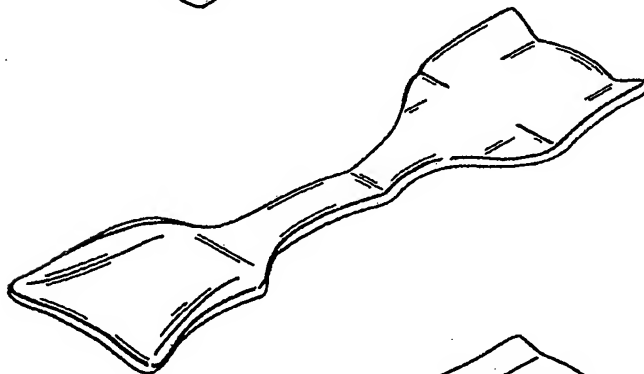


Fig. 1.3  
blended, 1% with  
polyethylene, treated  
according to Table 1,  
No. 3, after 3 days

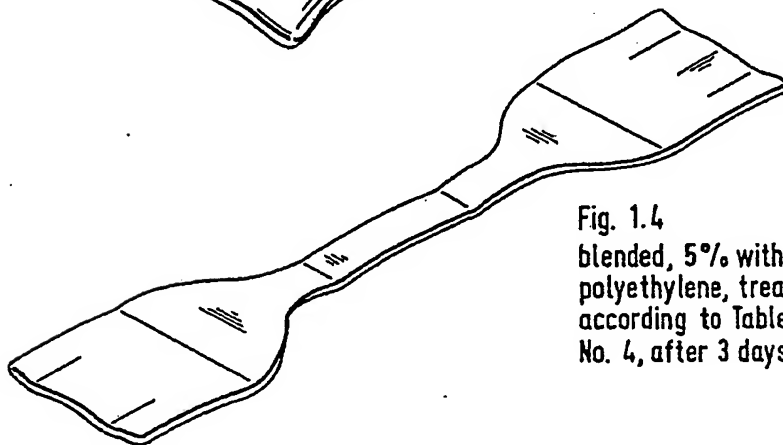


Fig. 1.4  
blended, 5% with  
polyethylene, treated  
according to Table 1,  
No. 4, after 3 days



**Fig. 2**

Comparative Testing, unblended starch versus starch blended with:

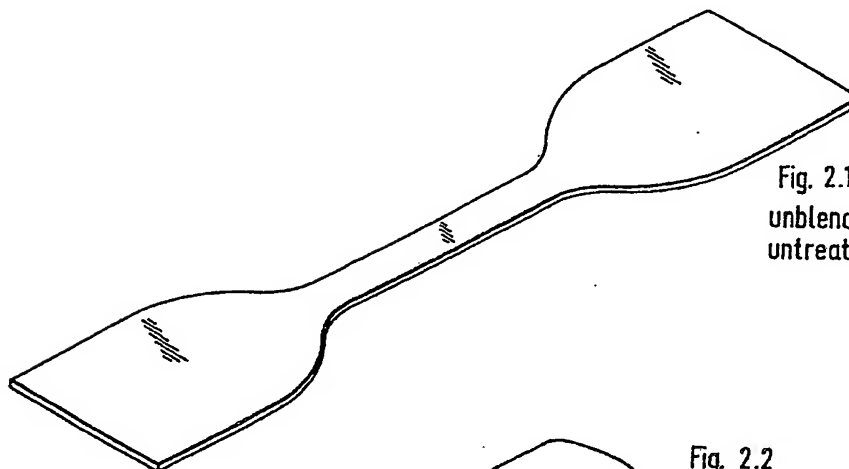


Fig. 2.1  
unblended or blended,  
untreated

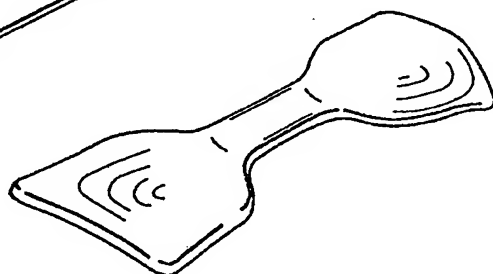


Fig. 2.2  
unblended,  
treated according to  
Table 1, No. 1 after  
3 days

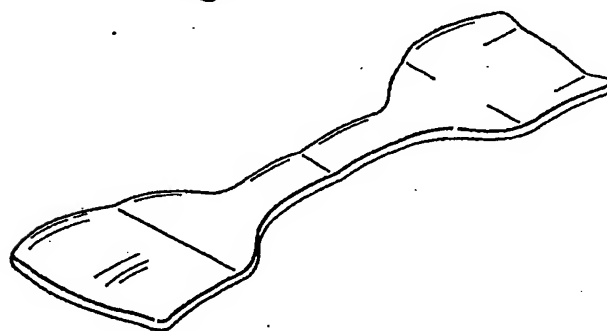


Fig. 2.3  
blended, 1% with  
polyacetal, treated  
according to Table 1,  
No. 8, after 3 days

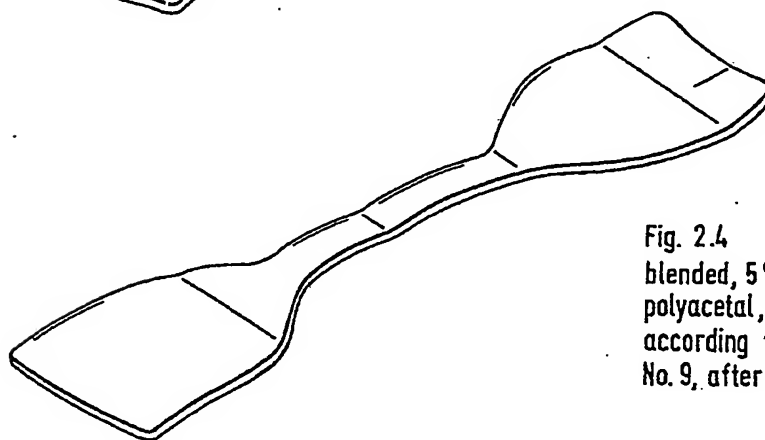


Fig. 2.4  
blended, 5% with  
polyacetal, treated  
according to Table 1,  
No. 9, after 3 days

Comparative Testing, unblended starch versus starch blended with:

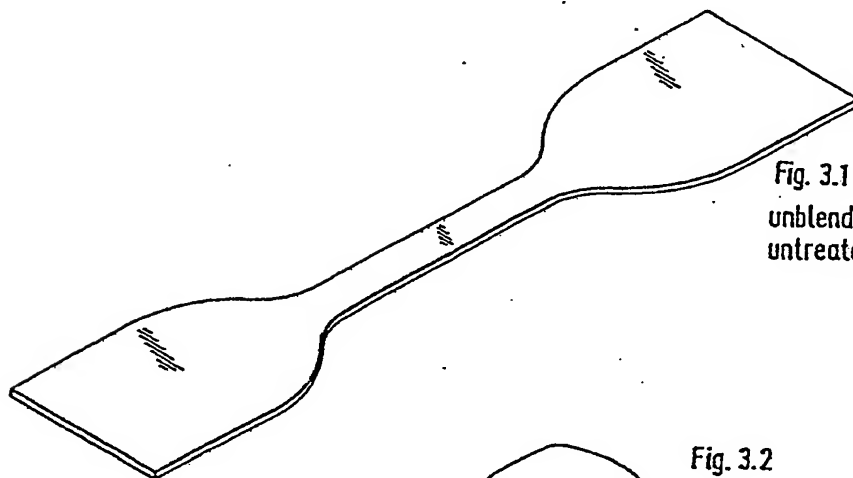


Fig. 3.1  
unblended or blended;  
untreated

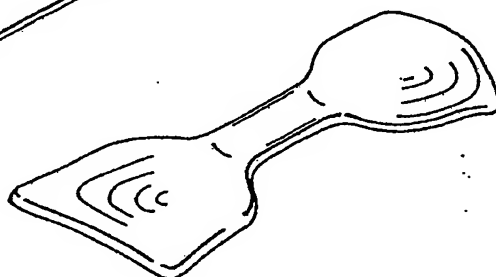


Fig. 3.2  
unblended,  
treated according to  
Table 1, No. 1 after  
3 days

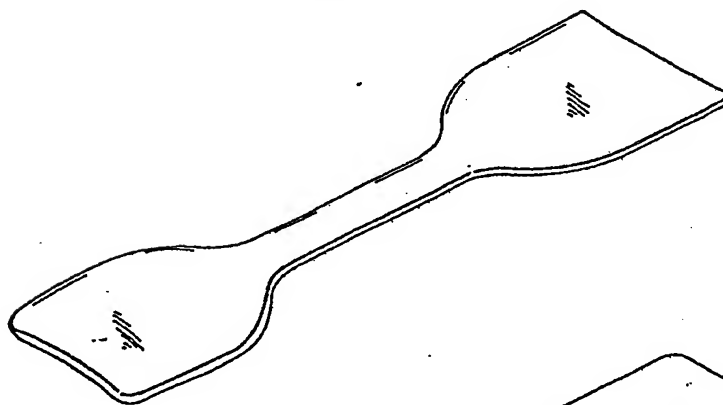


Fig. 3.3  
blended, 1% with  
ethylene acrylic  
acidcopolymer, treated  
according to Table 1,  
No. 13, after 3 days

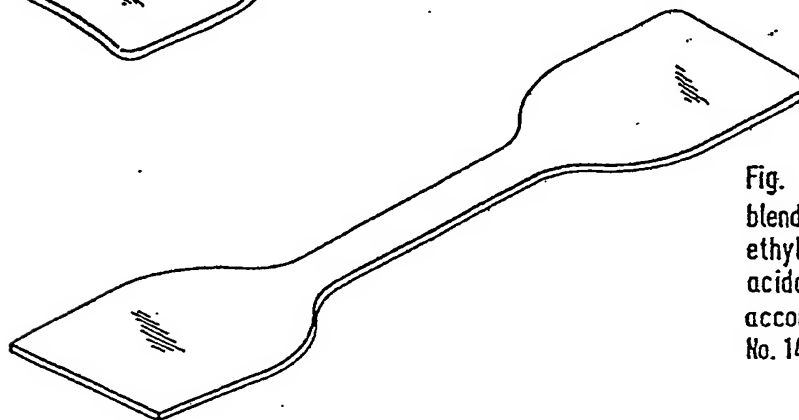


Fig. 3.4  
blended, 5% with  
ethylene acrylic  
acidcopolymer, treated  
according to Table 1,  
No. 14, after 3 days

**Fig. 4**

Comparative Testing, unblended starch versus starch blended with:

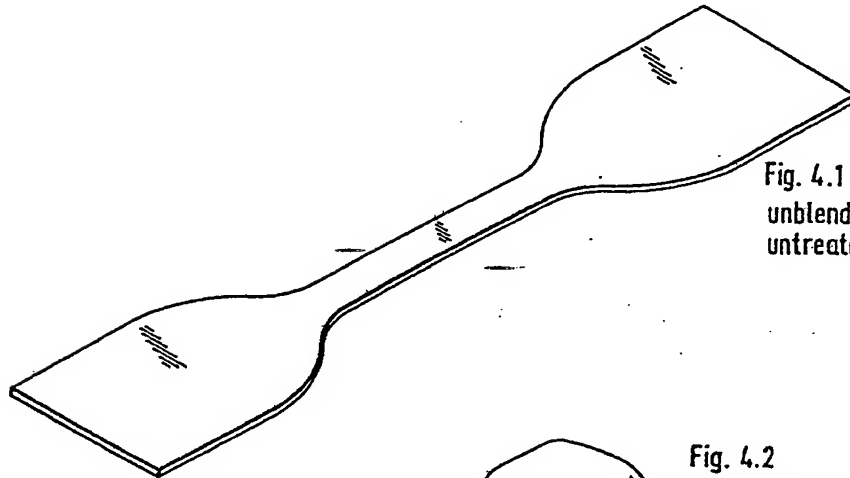


Fig. 4.1  
unblended or blended,  
untreated

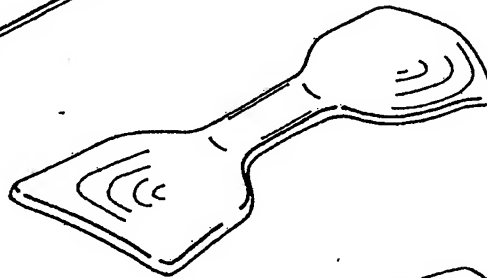


Fig. 4.2  
unblended,  
treated according to  
Table 1, No. 1 after  
3 days



Fig. 4.3  
blended, 1% with  
ethylene vinyl  
acetate copolymer,  
treated according  
to Table 1, No. 17,  
after 3 days

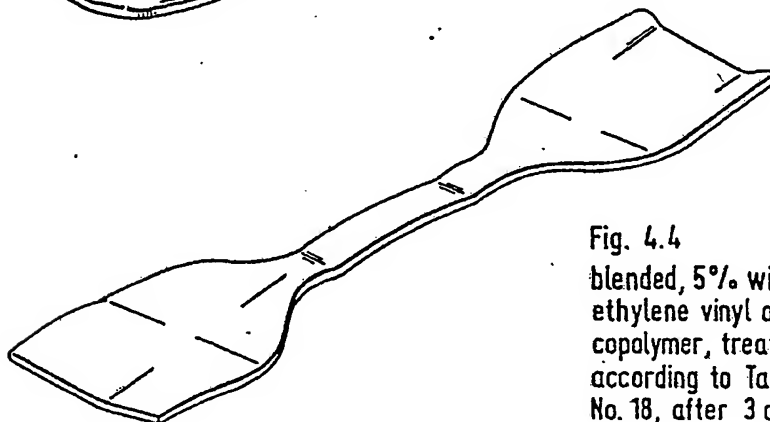


Fig. 4.4  
blended, 5% with  
ethylene vinyl acetate-  
copolymer, treated  
according to Table 1,  
No. 18, after 3 days